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MECHANISMS OF ACTIVATED CARBON DEGRADATION BY PERSPIRATION (CHL--ETC(U)
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PERSPIRATION (CHLORAMINE B THERMAL DECOMPOSITION
MECHANISMS)

DREXEL UNIVERSITY
PHILADELPHIA, PENNSYLVANIA

APRIL 1976

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MECHANISMS OF ACTIVATED CARBON DEGRADATION BY PERSPIRATION
(CHLORAMINE B THERMAL DECOMPOSITION MECHANISMS)

First Quarterly Progress Report

July 1975 to September 1975

by

Dr. Louis L. Pytlewski

April 1976

DREXEL UNIVERSITY

Philadelphia, Pa. 19104

Contract DAAA15-75-C-0195

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Sweat poisoning	Sweat solution	Phenyl sulfone
Activated carbon	Sweat studies	Benzenesulfonamide
Chloramine B.	Chloramine B hydrolysis	Oxygen
Thermal decomposition	Chloramine B ionization	Nitrogen
Chloramine B. Stability	Chloramine B disproportionation	Reaction mechanisms
		Differential scanning
		Calorimetry
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) At low temperature chloramine B reacts with H ₂ O to give N ₂ and O ₂ ; phenyl sulfone and benzenesulfonamide are formed. A neutral buffer represses or eliminates this hydrolysis. The dehydration of chloramine B is undesirable. Storage of hydrated salt in a sealed system is also undesirable. Storage of chloramine B at the lowest temperature possible is strongly recommended.		

PREFACE

The work described in this report was authorized under Project/Task 1W762710A09506, Physical Protection Against Chemical Agents; Body Protection Investigations. This work was started in July 1, 1975 and completed in September 30, 1975.

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MECHANISMS OF ACTIVATED CARBON DEGRADATION BY PERSPIRATION
(CHLORAMINE B THERMAL DECOMPOSITION MECHANISMS)

I. INTRODUCTION.

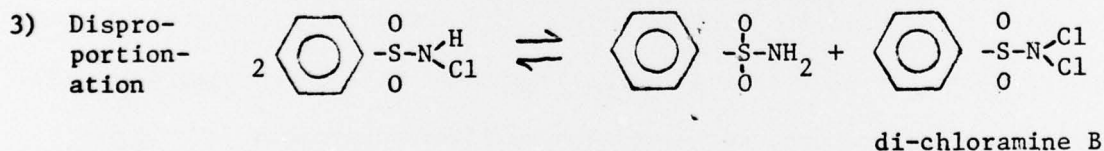
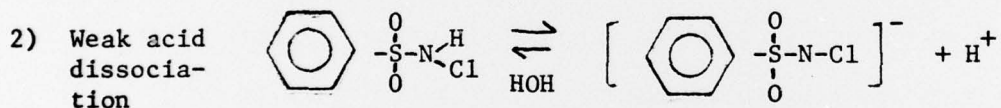
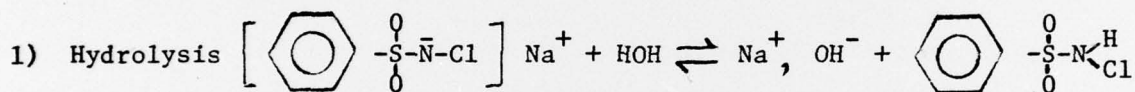
Although the contract time of effort was to focus on the sweat poisoning of activated carbon, a more urgent problem concerning the blowing apart of heated, sealed ampoules of chloramine B arose and we were asked to initially investigate this matter. This first quarterly period was occupied by two simultaneous experimental directions. Since we had just completed work on XXCC-3 we were already set up to look at chloramine B so that no undue preparations were required here. Our sweat studies required the use of a gas chromatograph, which had been ordered, and the acquisition of a sizeable variety of the more exotic chemicals for the construction of a synthetic sweat solution. During this waiting period we had designed a sizeable number of experiments for our sweat studies in anticipation of not losing a step by projecting a finish date for the chloramine B work to coincide with the beginning of the second quarter of this research period. Thus, this quarterly report contains our experimental work and conclusions on the thermal decomposition of chloramine B in the temperature range of room temperature to 100°C. The high temperature range is not reported here, even though the study was made, since this is of academic interest only. The research on the whole is now in manuscript form for publication in the Journal of Organic Chemistry and will be submitted, beforehand, for clearance by Edgewood Arsenal.

II. CHLORAMINE B - A STUDY OF ITS DECOMPOSITION.

There are two temperature ranges where decomposition occurs; the first is from room temperature to about 100°C, the second at about 175-185°C. The lower temperature decomposition appears to be associated with hydrolysis of the chloramine B salt. The higher temperature reaction is characteristic of N-Cl bond-compound burns - quite exothermic with considerable violence.

A. Low Temperature Range.

Chloramine B is the salt of a strong base and weak acid and is subject to aqueous equilibria as:

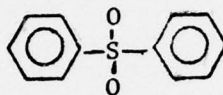


When chloramine B was carefully placed underwater so as not to dissolve the salt and left at room temperature, in about six hours a measurable amount of gas collected around a fiberglass plug. This gas was directly removed and analyzed using a gas chromatograph (GC) with the result that 91% was N₂ and 9% O₂. This experiment was repeated several

times and found quite reproducible. The solid at the bottom of the tube took on a deeper and deeper yellow-tan color. In fact, a yellow-tan precipitate separated from the chloramine B after a 24 hour period at room temperature.

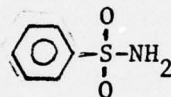
Infrared and mass spectrophotometry analyses of this precipitate indicated two components:

a) Phenyl sulfone



(a bright yellow solid)

b) Benzene sulfonamide



(colorless)

When the "chloramine B-underwater" experiment was conducted in an oil bath at a temperature of 60°C, there occurred a rapid evolution of gas initially which gradually ceased as the chloramine B went into solution. There was deposited a large amount of a water insoluble, deep brown solid which did not contain phenyl sulfone or benzene sulfonamide. This could be phenyl disulfone, and we are presently working on the analysis of this material.

With this experiment there was produced about 4-5 mls of gas per 9 grams of MSA chloramine B. The experiment was repeated using a NaCl solution in place of water. The results were exactly like those using distilled water. It was felt and proven erroneous later, that since NaCl is always one of the decomposition products at both the low and high temperature ranges that perhaps the addition of a NaCl solution to chloramine B would prevent or deter decomposition.

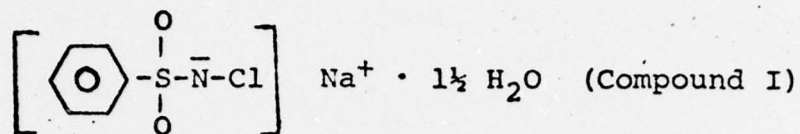
However, we were able to succeed in preventing the formation of gaseous products at 60°C by the use of a commercial pH 7 buffer solution over chloramine B. In fact the temperature on the system was raised to 95°C and,

after six hours at this temperature only 0.25 ml of gas collected (probably from dissolved air and/or CO_2 at this high temperature). The particular buffer solution used contained KH_2PO_4 and KOH . Since the addition of acidic and basic compounds, individually, appear to accelerate chloramine B decomposition in the lower temperature range it was felt that a neutral buffer might help to control the formation of both by hydrolysis i.e., greatly reduce the degree of hydrolysis and therefore enhance the lower temperature stability of chloramine B. At the moment we are mixing the appropriate amounts of KH_2PO_4 and KOH with chloramine B using the 12% H_2O present to give a "built in" pH buffer. This solid mixture will be heated and surveyed for decomposition. Additionally, a range of buffers will be studied for effectiveness.

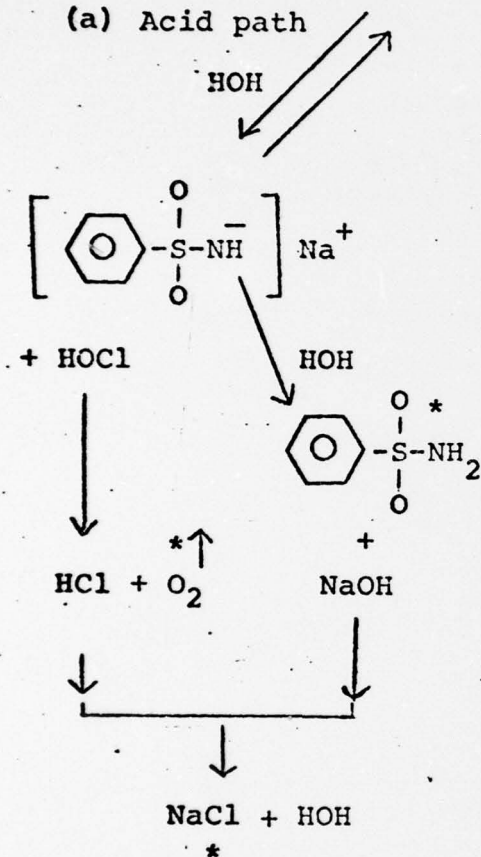
The evolution of N_2 and O_2 from heated chloramine B is best understood by considering several decomposition paths. The easiest to explain is the formation of O_2 . This must come from hydrolysis whereby the NaOH formed reacts with the N-Cl bond to give NaOCl . (The reverse of the method of synthesis). The hypochlorite ion disproportionates to give NaCl and O_2 . This process is assisted by the formation of water insoluble benzene-sulfonamide. An overall view of the lower temperature decomposition along with isolated and characterized products is as follows:

Reaction: Chloramine B - Room temperature to $\sim 100^\circ\text{C}$

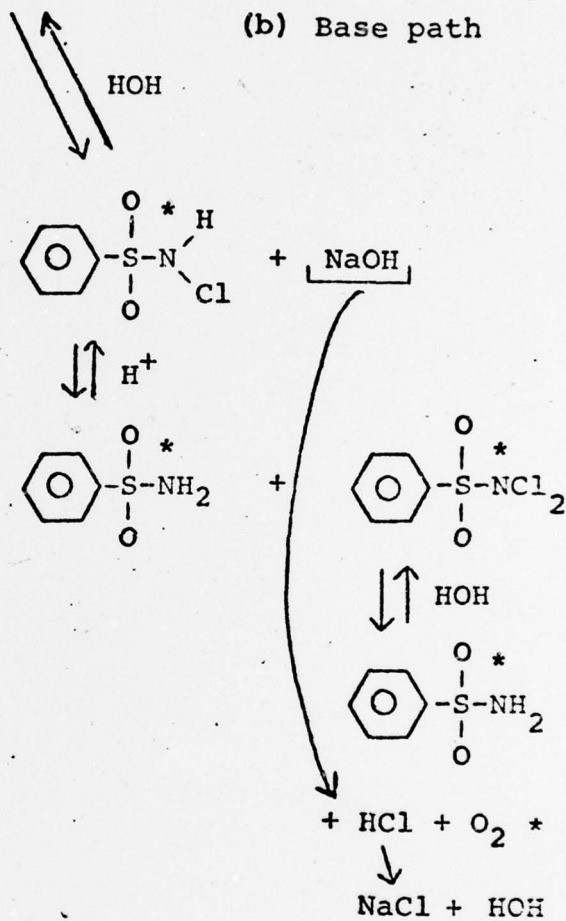
* = identified products to date



(a) Acid path

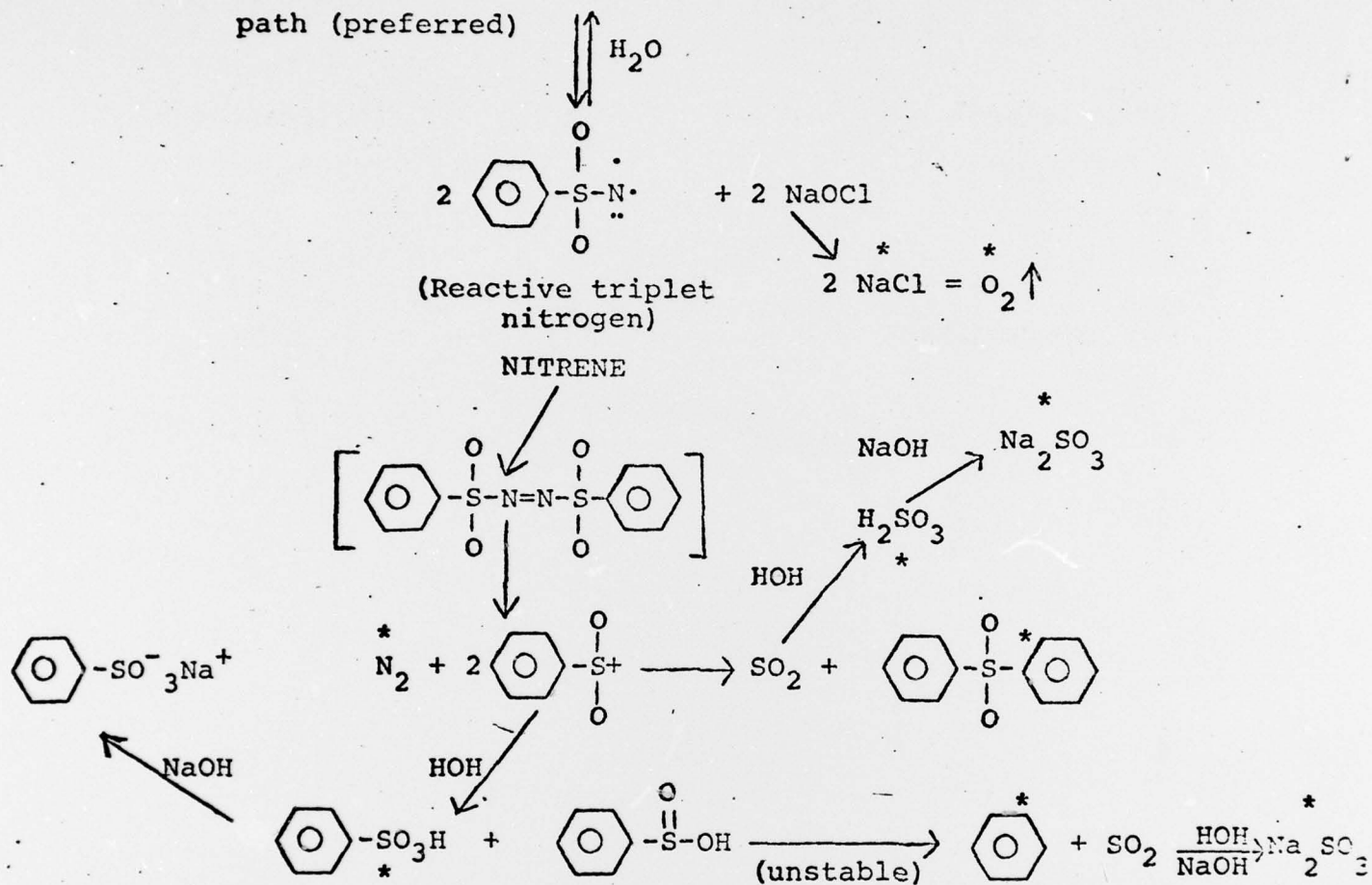


(b) Base path



(c) Dissociation
path (preferred)

Compound I



The total amount of gas evolved by chloramine B under water was quite small compared to the maximum amount possible if all the bound N were converted to N_2 . 18 gms of chloramine B could yield as much as 820 mls of N_2 (at S.T.P.). Our excess water experiments indicated about a 1% conversion to N_2 and O_2 by the hydrolysis route.

Fresh samples of chloramine B supplied to us by MSA did contain about 0.1% water insoluble material which we identified as phenyl sulfone (yellow-tan) and benzenesulfonamide. Each one of these compounds is not known to possess any unusual instability - dry or wet.

Attempts to isolate pure chloramine B by successive recrystallization only resulted in an increasing build up of insolubles (phenyl sulfone and benzenesulfonamide).

B. Higher Temperature Range.

Chloramine B was heated in an evacuated system at various temperatures up to about 185°C. The lower temperature range, discussed previously, produced a dehydration without the formation of N_2 and O_2 gas in measurable amounts. There was the appearance of NaCl in the solid (about 3% of the total weight) and the rest chloramine B. This material burned violently at the higher temperature (185°C) and H_2SO_3 collected in large amounts on the attached I.R. gas cell windows.

When chloramine B was heated in an open system, the acidity and basicity of the vapor phase was tested with moistened pH paper. The response was neutral until the sample burned at which point the paper indicated high acidity.

Differential Scanning Colorimetry measurements were made on MSA chloramine B. In the low temperature range only a broad endotherm was observed - the caloric value of this endotherm was close to that calculated for the vaporization of 12% water and was quite reproducible.

MSA reported a 20% loss in active chlorine after heating chloramine B in the lower temperature range. We feel that the mechanism involved in such a loss is the conversion of some of the chloramine B by partial hydrolysis to NaOCl with subsequent disproportionation to NaCl and O₂. If 18 gms. of chloramine B are contained in an ampule of 30 ml. volume then a 20% loss in active chlorine, per the above mechanism, would correspond to the evolution of 166 ml. of O₂ gas. This amount of O₂ would require only 14.2% of the water associated with chloramine B. At a temperature of 70°C this amount of oxygen alone would produce a pressure of 7.44 atmospheres in the 30 ml. volume glass ampoule (do not forget that the amount of N₂ evolved concurrently is roughly 10 times that of O₂).

III. CONCLUSIONS.

In the lower temperature range chloramine B reacts with water to evolve N₂ and O₂ with the formation of phenyl sulfone and benzenesulfonamide. If the water of crystallization is allowed to freely escape as heat is applied, the conversion of chloramine B to these aforementioned products is very small (negligible) but the dehydrated solid that remains is now capable of the higher temperature violent, exothermic burn which will occur at 70°C if enough time is given. If chloramine B is placed under water (large excess) then hydrolysis occurs to produce N₂, O₂, phenyl sulfone, and benzenesulfonamide but this reaction ceases rapidly at elevated temperature with the solution of chloramine B. It would seem from this that the worst possible system is that in which the water of crystallization is not allowed to escape and yet is not enough to cause solution of the chloramine B - such is the case of the MSA sealed ampoule. Even if only 14.2% of the water in the chloramine B is consumed by hydrolysis this will result in the production of a partial pressure of oxygen of over

7 atmospheres at 70°C.

As to prevention of this phenomenon the following are dictated by the available data to date:

- A. The repression or elimination of chloramine B hydrolysis - apparently a neutral buffer solution is effective here.
- B. Avoid dehydration and also storage of hydrated salt in a sealed system.
- C. If H_2O is necessary, then solutions of chloramine B appear safer by far at conditions other than those in #2 above - especially if the storage container can allow for a water vapor pressure blow-off and self-equilibration at elevated temperatures.
- D. All in all, storage of ampoules of chloramine B at lowest temperature possible is strongly recommended.